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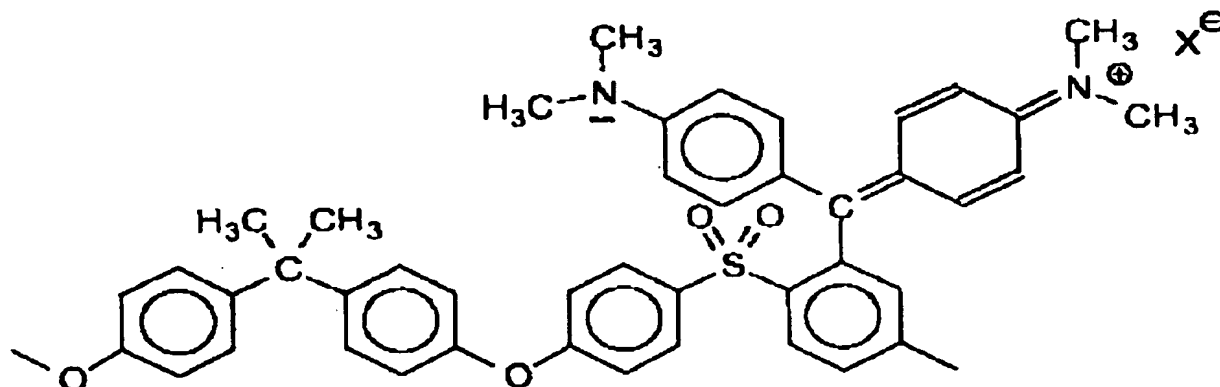
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(54) Title: POLYMER MEMBRANES



(57) Abrégé/Abstract:

The invention relates to novel organic/inorganic hybrid membranes which have the following composition: a polymer acid containing $-\text{SO}_3\text{H}$ -, $-\text{PO}_3\text{H}_2$ -, $-\text{COOH}$ - or $\text{B}(\text{OH})_2$ groups; a polymer base (optional), which contains primary, secondary or tertiary amino groups, pyridine groups, imidazole, benzimidazole, triazole, benzotriazole-pyrazole or benzpyrazole groups, either in the side chain or the main chain; an additional polymer base (optional) containing the aforementioned base groups; an elemental oxide, or metal oxide or metal hydroxide, which has been obtained by the hydrolysis and/or sol-gel reaction of one elemental organic and/or organometallic compound during the membrane forming process and/or by a re-treatment of the membrane in aqueous acidic, alkaline or neutral electrolytes. The invention also relates to methods for producing said membranes and to the various uses for membranes of this type.

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Abstract

The invention relates to novel organic/inorganic hybrid membranes which have the following composition: a polymer acid containing $-\text{SO}_3\text{H}$, $-\text{PO}_3\text{H}_2$, $-\text{COOH}$ or $\text{B}(\text{OH})_2$ groups, a polymeric base (optional), which contains primary, secondary or tertiary amino groups, pyridine groups, imidazole, benzimidazole, triazole, benzotriazole, pyrazole or benzopyrazole groups, either in the side chain or in the main chain; an additional polymeric base (optional) containing the aforementioned basic groups; an element or metal oxide or hydroxide, which has been obtained by hydrolysis and/or sol-gel reaction of an elementalorganic and/or metalorganic compound during the membrane forming process and/or by a re-treatment of the membrane in aqueous acidic, alkaline or neutral electrolytes. The invention also relates to methods for producing said membranes and to various uses for membranes of this type.

Amended claims

1. Composites and composite membranes, comprising (A) at least one polymeric acid, (B) one or more polymeric bases and (C1) at least nanodispersed element oxide and/or element hydroxide and/or metal oxide and/or metal hydroxide.
 2. Composites and composite membranes, comprising (A) at least one polymeric acid, (B) one or more polymeric bases and (C2) at least nanodispersed element phosphate and/or element hydrogenphosphate and/or element dihydrogenphosphate and/or metal phosphate and/or metal hydrogenphosphate and/or metal dihydrogenphosphate.
 3. Composites and composite membranes according to claim 1 and 2, characterized in that the polymeric acid is an aryl main chain polymer and comprises as acidic groups SO_3H , PO_3H_2 , COOH or $\text{B}(\text{OH})_2$ or their salts and is chosen from the group of polyethersulfones, polysulfones, polyphenyl sulfones, polyether ether sulfones, polyether ketones, polyether ether ketones, polyphenylene ethers, polydiphenylphenylene ethers, polyphenylene sulfides or is a copolymer, that contains at least one of these components.
 4. Composites and composite membranes according to claim 1 and 2, characterized in that the polymeric bases contain primary, secondary or tertiary amino groups, pyridine groups, imidazole, benzimidazole, triazole, benzotriazole, pyrazole or benzopyrazole groups either in the side chain or in the main chain.
 5. Composites and composite membranes according to one or more of claims 1 to 4, characterized in that they contain a salt, elemental or metal oxide or metal hydroxide, which has been obtained by hydrolysis and/or sol/gel reaction after membrane formation and is characterized in that the non-hydrolyzed precursor(s) of the salt, element or metal oxide or metal hydroxide is (are) added to the polymeric acid and the polymeric base(s) prior to removal of the solvent.
 6. Non-hydrolyzed precursors of claim 5 characterized in that they are chosen from:
 - metal/element alkoxides/esters of Ti, Zr, Sn, Si, B, Al,
 - metal acetylacetonates, e.g. $\text{Ti}(\text{acac})_4$, $\text{Zr}(\text{acac})_4$,
 - mixed compounds of metal/element alkoxides, and metal acetylacetonates, e.g. $\text{Ti}(\text{acac})_2(\text{OiPr})_2$ etc.,
-

organic amino compounds of Ti, Zr, Sn, Si, B, Al,

7. Composites and composite membranes according to claim 1, 2 and/or 5, characterized in that they are additionally covalently cross-linked.
8. Composite membranes according to claim 5 and 7, characterized in that the membranes are posttreated with phosphoric acid to generate in the membrane matrix from the metal oxides and/or metal hydroxides and/or metal oxide hydroxides metal or element phosphates or hydrogenphosphates or dihydrogenphosphates, which contribute to proton conductivity.
9. Process for the preparation of composites and composite membranes according to one or more of claims 1 to 8, characterized in that the following components are mixed in a dipolar-aprotic solvent such as N-methylpyrrolidinone (NMP), N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), dimethylsulfoxide (DMSO) or sulfolane: a polymeric acid with SO_3X , PO_3X_2 , COOX or $\text{B}(\text{OX})_2$ ($\text{X}=\text{H}$, univalent or bivalent or trivalent or tetravalent metal cation), at least one polymeric base which carries primary, secondary or tertiary amino groups, pyridine groups, imidazole, benzimidazole, triazole, benzotriazole, pyrazole or benzopyrazole groups either in the side chain and/or the main chain, and at least metalorganic or elementorganic compounds according to the compounds of claim 6.
10. Process according to claim 9, characterized in that the polymer solution of claim 9 is cast in thin films onto a support (glass plate or metal plate, tissue, wovens, non-wovens, fleece, porous (polymer)membrane), the solvent is evaporated at temperatures of from 80 to 150°C at normal pressure or under vacuum, and the formed thin film is cured as follows, whereby the order of posttreatment steps can vary and also optionally the steps (1) and/or (2) and/or (3) can be omitted:
 - in water at $T=50$ to 100°C
 - in 1 to 100% mineral acid (hydrokalic acid, sulfuric acid, phosphoric acid) at $T=50$ to 100°C
 - in 1 to 50% aqueous base (e.g. ammonia solution, amine solution, sodium hydroxide solution, potassium hydroxide solution, sodium carbonate solution, calcium hydroxide solution, barium hydroxide solution) or in an anhydrous liquid amine or a mixture of different liquid amines.
 - in water at $T=50$ to 100°C .

11. Process for the preparation of composites and composite membranes, characterized in that the following components are mixed in a dipolar-aprotic solvent such as N-methylpyrrolidinone (NMP), N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), dimethylsulfoxide (DMSO) or sulfolane: a polymeric acid with SO_3X , PO_3X_2 , COOX or $\text{B}(\text{OX})_2$ (X =univalent or bivalent or trivalent or tetravalent metal cation), at least one polymeric base which carries primary, secondary or tertiary amino groups, pyridine groups, imidazole, benzimidazole, triazole, benzotriazole, pyrazole or benzopyrazole groups either in the side chain and/or in the main chain, and at least metalorganic or elementorganic compounds according to the compounds of claim 6, characterized in that the polymer solution of claim 9 is cast in thin films onto a support (glass-plate or metal plate, tissue, fleece, porous (polymer)membrane), the solvent is evaporated at temperatures of from 80 to 150°C at normal pressure or under vacuum and the formed thin film is posttreated in water at $T=50$ to 100°C.
 12. Use of membranes according to claim 1 and/or 2 to produce energy by an electrochemical way.
 13. Use of membranes according to claim 1 and/or 2 as component in membrane fuel cells (H_2 - or direct methanol fuel cells) at temperatures from 0 to 180°C.
 14. Use of membranes according to claim 1 and/or 2 in electrochemical cells.
 15. Use of membranes according to claim 1 and/or 2 in secondary batteries.
 16. Use of membranes according to claim 1 and/or 2 in electrolysis cells.
 17. Use of membranes according to claim 1 and/or 2 in membrane separation processes such as gas separation, pervaporation, perstraction, reverse osmosis, electrodialysis and diffusion dialysis.
-

Polymer membranes

The invention relates to novel organic/inorganic hybrid membranes which have the following composition:

- 5 • a polymeric acid containing $-\text{SO}_3\text{H}$, $-\text{PO}_3\text{H}_2$, $-\text{COOH}$ or $\text{B}(\text{OH})_2$ groups
- a polymeric base (optional), which contains primary, secondary or tertiary amino groups, pyridine groups, imidazole, benzimidazole, triazole, benzotriazole, pyrazole or benzopyrazole groups either in the side chain or in the main chain.
- an additional polymeric base (optional) containing the aforementioned basic groups
- 10 • an element or metal oxide or hydroxide, which has been obtained by hydrolysis and/or sol-gel reaction of an elementorganic and/or metalorganic compound during the membrane forming process and/or by posttreatment of the membrane in aqueous acidic, alkaline or neutral electrolytes.

15 The invention also relates to methods for producing said membranes and to various uses for membranes of this type.

The state-of-the-art regarding ionomer/inorganic hybrid composites is exposed in the review of Mauritz, who is one of the pioneers of the implementation of sol/gel technique in organopolymers, and especially in ionomers such as Nafion® (Organic-inorganic hybrid materials: perfluorinated ionomers as sol-gel polymerization templates for inorganic alkoxides K. A. Mauritz Mat. Sci. Eng. C 6 (1998) 121-133). Core of the process is the hydrolysis of an elementorganic or metalorganic compound in the matrix of an ionically functionalized organopolymer to an element or metal oxide or hydroxide network.

25 Further examples of systems described in the literature are:

- (a) Nafion® is preswollen in water and alcohol and then immersed in tetraethoxysilane(TEOS)/alcohol solutions. In the sulfonic acid clusters of the Nafion membrane then a sol-gel reaction takes place catalyzed by the sulfonic acid protons, from TEOS to SiO_2/OH networks containing water („nanocomposites“) (Microstructural evolution of a Silicon Oxide Phase in a Perfluorosulfonic Acid ionomer by an In Situ Sol-Gel Reaction, K. A. Mauritz, I. D. Stefanithis, S. V. Davis, et al. J. Appl. Polym. Sci. 55, 181-190 (1995)).
- (b) Nafion® is preswollen in water and alcohol and then immersed in alcohol solutions of $\text{Zr}(\text{OBu})_4$. In the sulfonic acid clusters of the Nafion membrane then a sol-gel reaction takes place catalyzed by the sulfonic acid protons, from $\text{Zr}(\text{OBu})_4$ to ZrO_2 networks containing water („nanocomposites“) (Asymmetric Nafion/(Zirconium Oxide) Hybrid Membranes via In

Situ Sol-Gel Chemistry, W. Apichatachutapan, R. B. Moore, K. A. Mauritz, J. Appl. Polym. Sci. 62, 417-426 (1996)).

(c) Nafion sulfonyl fluoride precursor membranes are preswollen in perfluorohydrophenanthrene and immersed in 3-aminopropyltriethoxysilane. Thereafter excess silane is washed out with EtOH. Hybrids are formed, in which, by hydrolysis of said silane and by reaction of said silane with SO₂F-groups, SiO₂-networks partially cross-linked with the polymer are formed in the membrane matrix (Chemical modification of a nafion sulfonyl fluoride precursor via in situ sol-gel reactions, A. J. Greso, R. B. Moore, K. M. Cable, W. L. Jarrett, K. A. Mauritz, Polymer 38, 1345-1356 (1997).

(d) Surlyn® ionomer membranes in the Zn²⁺ form are swollen in 1-propanol and then immersed in H₂O/TEOS mixtures. In the membrane matrix then a sol-gel reaction takes place catalyzed by the sulfonic acid protons, from TEOS to SiO₂/OH networks containing water („nanocomposites“) (Surlyn®/[Silicon Oxide] Hybrid Materials. 2. Physical Properties Characterization, D. A. Siuzdak, K. A. Mauritz, J. Polym. Sci. Part B: Polymer Physics, 37, 143-154 (1999).

A disadvantage of the known systems (a) to (d) is, that the sol-gel reaction takes place in a preformed membrane and consequently the content of an inorganic polymer phase formed by hydrolysis, of the polymer composite can not be set at will.

Also hybrid systems of nonionic polymers and metal or element oxides are described in the literature:

(e) composites of poly(n-butylmethacrylate) and titanium oxide, made by water vapor hydrolysis of titanium alkoxides, which had been added to alcoholic solutions of a poly(n-butylmethacrylate) polymer solution, in the polymer matrix after evaporation of the solvent. (Novel Poly(n-Butyl Methacrylate)/Titanium Oxide Alloys Produced by the Sol-Gel process for Titanium Alkoxides, K. A. Mauritz, C. K. Jones, J. Appl. Polym. Sci. 40, 1401-1420 (1990)).

(f) composite membranes of polyetherimide and nanodispersed silicium oxide, made by hydrolysis of TEOS in solutions of polyetherimide Ultem® in NMP by adding of 0.15 M HCl solution. After hydrolysis dense or phase inversed membranes are made from this polymer solution. Compatibility of the inorganic with the organic phase was obtained by extra addition of 3-aminopropyltrimethoxysilane (AS) (Membranes of poly(ether imide) and nanodispersed silica, S. P. Nunes, K. V. Peinemann, K. Ohlrogge, A. Alpers, M. Keller, A. T. N. Pires, J. Memb. Sci. 157 (1999) 219-226)).

These systems present similar disadvantages as already described previously.

As the descriptions show, there are already a number of pure organic and also provided with inorganic additives proton conducting membranes, however all of these systems and membranes present poor thermal and mechanical stability, which especially impinges on regions above a temperature of 100 °C.

Consequently an object of the invention is to provide novel composites and composite membranes of mixtures of cation exchange polymers and basic polymers additionally containing an inorganic element/metal oxide/hydroxide phase, which improves the following membrane properties:

- mechanical stability
- thermal stability
- improved water holding ability even at temperatures of > 100 °C, which is important in particular for the application in membrane fuel cells in the temperature range > 100 °C.

This object is solved by providing membranes according to claim 1.

Furthermore the process according to the invention contributes to solve this object.

Herein organic precursors of element/metal oxides/hydroxides are brought into the polymer solution (alkoxide/ester, acetylacetonate etc).

The formation of the inorganic phase in the ionomer happens after the membrane formation by hydrolysis in acidic, alkaline and/or neutral aqueous environment.

Surprisingly it has been found, that if Ti diacetylacetonate diisopropylate/ isopropanol is brought into solutions of the salt form of sulfonated poly(etheretherketone) sPEEK and a basic polymer (e.g. polybenzimidazole PBI Celazol®) in NMP or DMAc, the Ti diacetylacetonate diisopropylate does not hydrolyze in the polymer solution, but is built into the membrane matrix on evaporating of the solvent. Surprisingly it has been found, that the organic Ti compound can be hydrolyzed by successive posttreatment of the membrane in aqueous lye and/or water and/or acid via sol/gel reaction to titanium oxide nanodispersed in the membrane matrix. The titanium oxide can be identified by EDX in the membrane matrix. Thereby contents of TiO₂ in the membrane matrix of up to 35 weight % can be reached.

The composites according to the invention consist of:

- a polymeric acid with -SO₃H, -PO₃H₂, -COOH or B(OH)₂ groups, preferentially with an aryl main chain polymer backbone

- (optionally) one or two polymeric bases which carry primary, secondary or tertiary amino groups, pyridine groups, imidazole, benzimidazole, triazole, benzotriazole, pyrazole or benzopyrazole groups either in the side chain and/or in the main chain.
 - an element or metal oxide or hydroxide, obtained by hydrolysis of the following classes of elementorganic and/or metalorganic compounds:
 - metal/element alkoxide/ester of Ti, Zr, Sn, Si, B, Al
 - metal acetylacetonates, e.g. $\text{Ti}(\text{acac})_4$, $\text{Zr}(\text{acac})_4$
 - mixed compounds of metal/element alkoxides and metal acetylacetonates, e.g. $\text{Ti}(\text{acac})_2(\text{OiPr})_2$ etc.
 - organic amino compounds of Ti, Zr, Sn, Si, B, Al
- and are producible during the membrane formation process and/or by posttreatment of the membrane in aqueous acidic, alkaline or neutral electrolytes.

Due to the nanodispersed inorganic phase brought into the membrane matrix according to the invention the profile of properties of the ionomer(blend)membranes according to the invention is strongly improved.

The new inorganic/organic hybrid acid base blend membranes according to the invention show an excellent profile of properties:

- good proton conductivity
- excellent thermal stability
- excellent mechanical stability
- limited swelling.

Especially the water holding abilities of the membrane especially at $T > 100^\circ\text{C}$ are strongly improved. This is achieved by the inorganic oxide/hydroxide, which is present in the membrane in nanodispersed distribution of the inorganic component. By mixing of oxide powders into ionomer membranes, as has already been proposed in some publications (Comparison of Ethanol and Methanol Oxidation in a Liquid-Feed Solid Polymer Electrolyte Fuel Cell at High Temperature A. S. Arico, P. Creti, P. L. Antonucci, V. Antonucci, Electrochem. Sol. St. Lett. 182) 66-68 (1998)), such a fine distribution of the inorganic component in the membrane matrix as with the method according to the invention, wherein the elementorganic / metalorganic compounds are hydrolyzed to the oxide only in the membrane matrix, can not be reached. Thereby the membranes according to the invention show still further advantages:

- reduced methanol permeability
- contribution to proton conductivity, especially at $T > 100^\circ\text{C}$

The invention shall be exemplified by some examples as follows.

5 Preparation of ionomer blend membrane TJ-3

2 g of sulfonated polyether ether ketone Victrex® (ion exchange capacity 1,364 meq SO₃H/g) are dissolved in 10 g N-Methylpyrrolidinone. Subsequently 1 g of triethylamine is added to the solution to neutralize the sulfonic acid groups of the sPEEK. Hereafter 77 mg of poly(4-vinylpyridine) are added to the solution. After dissolution 5.1 g titanium(IV) bis(acetylacetonato) diisopropylate, 75 weight % solution in isopropanol, are added to the solution. Then the polymer solution film is degassed and then cast onto a glass-plate by a doctor knife to a 800 µm thick film. In a membrane dryer the solvent is removed at 100°C. After film drying the glass-plate with the polymer film is immersed in a tub with H₂O. The film peels off from the glass-plate. The film is posttreated for 24 h at 70°C in 1N NaOH, and then 24 h at 70°C in deionized water. Hereafter the film is stored at room temperature in deionized water. For the determination of the proton conductivity the film is equilibrated for 24 h in 0,5 N H₂SO₄ at room temperature.

20 *Characterization results:*

Film thickness[µm]:	100
IEC [meq SO ₃ H/g]:	1.15
Swelling [%]:	104
Permselectivity (0,5 N/ 0.1 N NaCl) [%]:	78.35
25 $R_{sp}^{H^+}$ (0.5 N HCl) [Ω cm]:	6.4
$R_{sp}^{H^+}$ (H ₂ O) [Ω cm]:	16.9
$R_{sp}^{Na^+}$ (0.5 N NaCl) [Ω cm]:	29.6

In Fig. 1 the EDX spectrum of the TJ3 membrane is shown. The Ti signal is clearly visible.

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Preparation of ionomer blend membrane JOA-2

3 g of sulfonated poly(etheretherketone) Victrex® (ion exchange capacity 1,75 meq SO₃H/g) are dissolved in 15 g N-Methylpyrrolidinone. Hereafter 0.5 g of n-propylamine are added to the solution to neutralize the sulfonic acid groups of the sPEEK. Hereafter 0.15 g of polymer 1 (Fig. 2) are added to the solution. Hereafter 1.4 g of 10.72 weight % PBI Celazol® (Fig. 3)

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solution are added to the solution. Hereafter 4.036 g titanium(IV) bis(acetylacetonato) diisopropylate, 75 weight % solution in isopropanol, are added to the solution. Hereafter the polymer solution film is degassed and then cast onto a glass-plate with a doctor knife to a 800 μm thick film. In a vacuum drying oven the solvents are removed first for 1 h at 75°C and 800 mbar and then at 120°C and at a pressure of first 800 mbar and then down to 50 mbar. After film drying the glass-plate with the polymer film is immersed in a tub with H_2O . The film peels off from the glass-plate. The film is posttreated for 24 h at 70°C in 1N NaOH, and then for 24 h at 70°C in deionized water. Thereafter the film is stored at room temperature in deionized water. For the determination of the proton conductivity the film is equilibrated for 24 h in 0,5 N H_2SO_4 at room temperature.

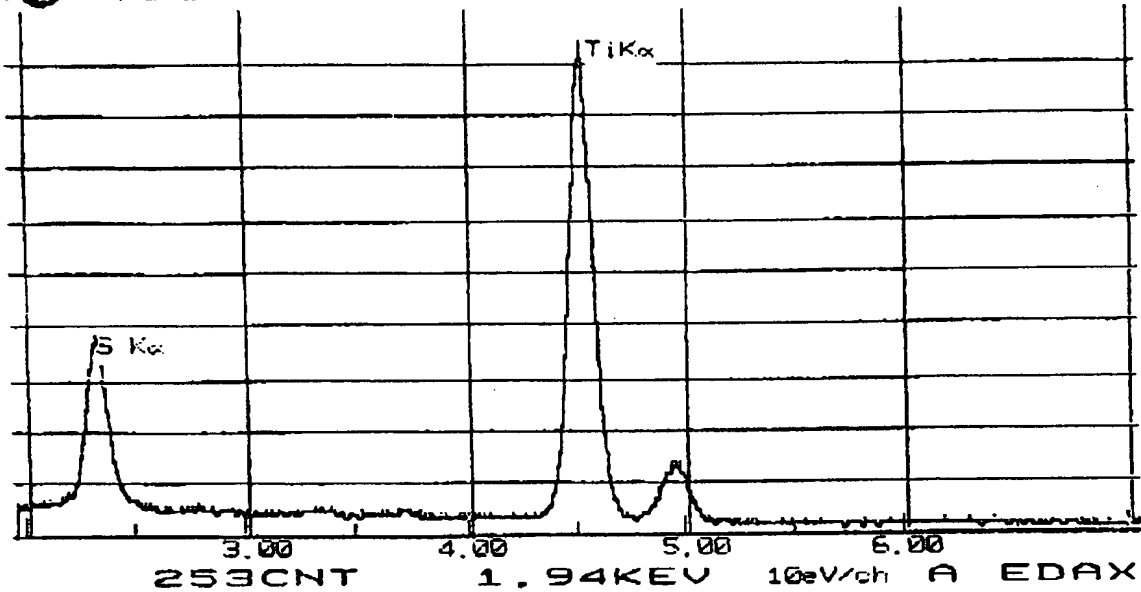
Characterization results:

Film thickness [μm]:	100
IEC [meq $\text{SO}_3\text{H/g}$]:	0.97
Swelling [%]:	27.7
Permselectivity [%]:	94.9
$R_{\text{sp}}^{\text{H}^+}$ (0.5 N H_2SO_4) [$\Omega \text{ cm}$]:	21.8
$R_{\text{sp}}^{\text{H}^+}$ (H_2O) [$\Omega \text{ cm}$]:	55.6
$R_{\text{sp}}^{\text{Na}^+}$ (0.5 N NaCl) [$\Omega \text{ cm}$]:	79

In Fig. 4 the EDX spectrum of the JOA-2 membrane is shown. The Ti signal is clearly visible.

Drawings

19-OCT-99 16:00:06 SUPER QUANT
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5 Fig. 1: EDX spectrum of TJ3 membrane

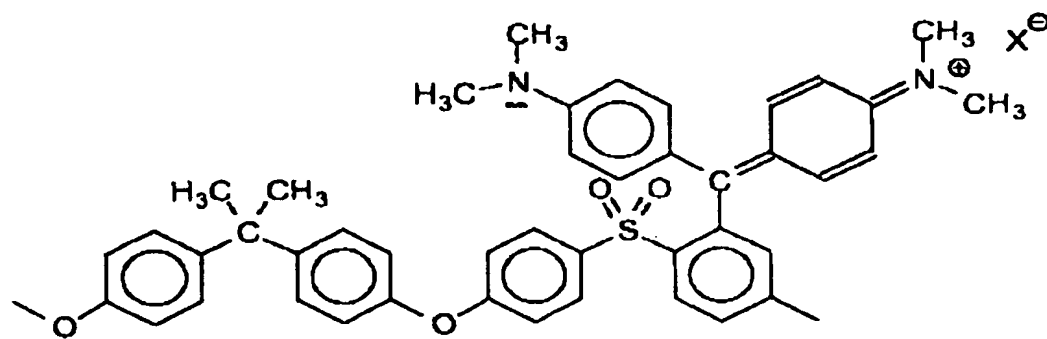


Fig. 2: polymer 1

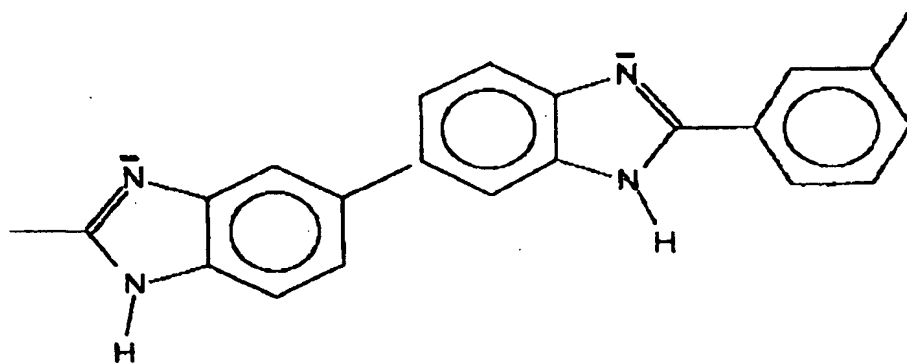


Fig. 3: PBI Celazol®

26-OCT-99 15:36:49 SUPER QUANT
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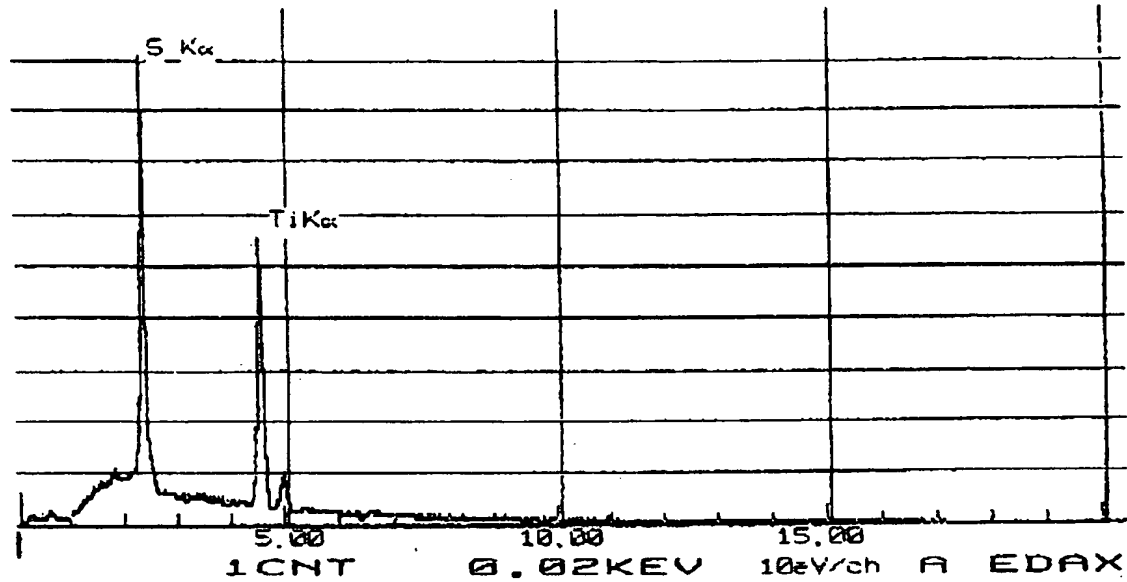


Fig. 4: EDX spectrum of JOA-2 membrane